

## Interaction Study of a new Bis-Bidentate Schiff's Base with some Metal Ions and its Application in Fabrication of Sm(III) Potentiometric Membrane Sensor

Mohammad Reza Ganjali<sup>1,\*</sup>, Mehdi Tavakoli<sup>1</sup>, Farnoush Faridbod<sup>1</sup>, Siavash Riahi<sup>2</sup>, Parviz Norouzi<sup>1</sup> and Masoud Salavati-Niassari<sup>3</sup>

<sup>1</sup> Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

<sup>2</sup> Institute of Petroleum Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran

<sup>3</sup> Department of Chemistry, Kashan University, Kashan, Iran

\*E-mail: [ganjali@khayam.ut.ac.ir](mailto:ganjali@khayam.ut.ac.ir)

Received: 25 September 2008 / Accepted: 24 October 2008 / Published: 17 November 2008

---

Theoretical and computational models are capable of reliably predicting ligand selectivity toward variety of metal ions which can be valuable tools for the advancement of practical works. According to the theoretical calculations and conductance studies, complexation of a new bis-bidentate schiff's base, 2-[[4-[[3-[(z)-1-(2-hydroxy phenyl) methylidene] amino]phenyl]oxy]phenyl]imino) methyl]-1-benzenol (APOPIB) with some mono, di and trivalent metal ions was investigated. Since APOPIB was able to form a selective complex with Sm(III) ion ( $K_f=5.23\pm 0.24$ ), it was applied as a sensing material in a poly vinyl chloride (PVC) membrane sensor for determination of Sm(III) ions. This sensor with the membrane composition of 30% PVC, 62% nitrobenzene (NB), 5% ionophore and 3% sodium tetraphenylborate (NaTPB), exhibits a rapid and good Nernstian response toward Sm(III) ions in the range of  $10^{-6}$  to  $10^{-1}$  mol L<sup>-1</sup> with a slope of  $19.3\pm 0.2$  mV per decade and a detection limit of  $6.1\times 10^{-7}$  mol L<sup>-1</sup>. The sensor can be used in a pH range from 5.5 to 9.5, the potential response of the sensor remained constant despite the pH fluctuations. The proposed sensor was evaluated by determining the samarium ion concentration at using a Certified Reference Material (CRM).

---

**Keywords:** complexation; sensor; samarium; potentiometry; membrane

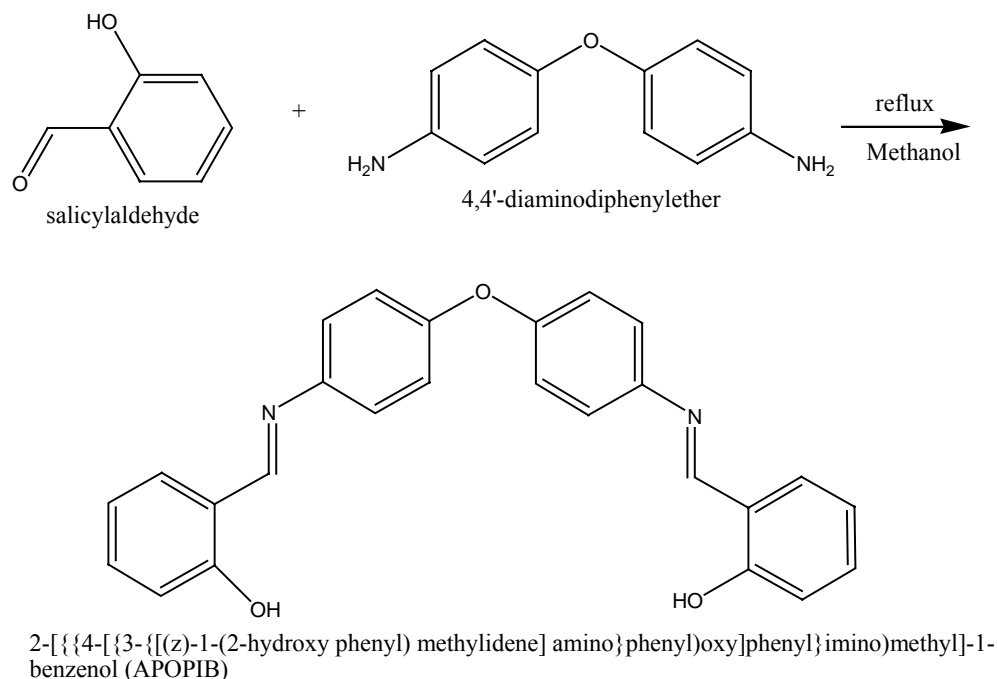
### 1. INTRODUCTION

The interest in constructing lanthanide sensors arises because they have similar ionic radii to calcium, but a higher charge density, which causes they are used as probes to find the interactions between Ca<sup>2+</sup> and biologically important molecules [1].

Today, many techniques have been used for the samarium determination such as inductive-coupled plasma atomic emission spectroscopy (ICP-AES) [2] cathode-ray-excited emission spectroscopy [3] and laser-excited atomic fluorescence spectrometry [4].

However, the utility of ion-selective electrodes (ISEs) is being increasingly realized by analytical chemists in view of the rapid growth of industry and technology all over the world, as they represent a rapid, accurate and low-cost method of analysis [5-9].

The major problem in the field of lanthanide potentiometric membrane sensors was finding a suitable and selective sensing material for using in the membrane. This series of elements has 15 members, which are rather similar. Having different radii of the lanthanum ions (from  $Ce^{3+}$  to  $Lu^{3+}$  their radii vary from 1.02 to 0.80 Å, respectively) causes their different properties, such as charge densities and hydration energy (from  $Ce^{3+}$  to  $Lu^{3+}$  their hydration energy ranges from 3370 to 3760 kJ/mol) [10]. Thus, the only way to design an ion-selective electrode for the lanthanide ions is using ionophores having semi cavity, heteroatoms (N, O and S as donor atoms), and high flexibility [6,11]. Such an ionophore can easily form a template with reference to the size of the cation [12-14]. Furthermore, these kinds of ionophores are able to form a stronger complex with one of the lanthanide cations than the other ones with the optimum free energies. As it can be seen from the recently reported lanthanide sensors [15-33], this phenomenon can be attributed to the type, the number and the site of its donor atoms, its flexibility as well as the size and the charge density of the cation.



**Figure 1.** Synthesis of bis-bidentate Schiff-base ligands

Schiff's base compounds refer to the branch of supramolecules that can be used as sensing material in the construction of potentiometric ion-selective electrodes for lanthanide series [5]. A Schiff's base (or azomethine or imine), named after Hugo Schiff (German Chemist, 1834-1915), is a

functional group with the general formula of  $R_1R_2C=N-R_3$ . These bases can be synthesized from an aromatic amine and a carbonyl compound (e.g. aldehydes, ketones) by nucleophilic addition, forming a hemiaminal, and followed by a dehydration to generate an imine. An imine (Schiff's base) particularly binds metal ions via the two donor atoms N and O. The steric and electronic effect around the metal core can be finely tuned by an appropriate selection of electron withdrawing or electron donating substituents, incorporated into the Schiff's bases [5].

Theoretical calculation and conductance study for complexation, showed the tendency of the new synthesized bis-bidentate Schiff's base, 2-[[4-[[3-[(z)-1-(2-hydroxy phenyl) methylidene] amino]phenyl]oxy] phenyl]imino) methyl]-1-benzenol (APOPIB) (Fig. 1) to selective complexation with Sm(III) ions, one of the lanthanide member.

## 2. EXPERIMENTAL PART

### 2.1. Apparatus

For the conductivity measurements, a Metrohm 660 conductivity meter and a black platinum dip-type conductivity cell (with a  $0.83 \text{ cm}^{-1}$  cell constant) were used.

The glass cell, where the  $\text{Sm}^{3+}$  ion-selective electrode was placed, consisted of an R684 model Analion Ag/AgCl double junction reference electrode as the internal reference electrode and a double-junction saturated calomel electrode (SCE, Philips). The cell chamber was filled with an ammonium nitrate solution and both electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with  $\pm 0.1 \text{ mV}$  precision.

### 2.2. Reagents and materials

Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), Benzyl acetate (BA), high relative molecular weight poly vinyl chloride (PVC), sodium tetraphenyl borate (NaTPB), and tetrahydrofuran (THF) were purchased from Merck and used as received. The acetic acid, furan-2-carboxylic acid hydrazide, pyridine-2-carbaldehyde, chloride and nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available and used without any further purification. Triply distilled deionized water was used throughout.

### 2.3. Synthesis of bis-bidentate Schiff-base ligands

The bis-bidentate ligands were prepared by a usual Schiff's base condensation in methanol (50 mL) of salicylaldehyde (10 mmol, 1.22 g) with bridging diamine (4,4'-diaminodiphenylether, 5 mmol, 1.00 g), Fig. 1. The solutions were stirred and refluxed for 12 h. Yellow precipitates were filtered, washed by a small amount of methanol and dried in vacuo.  $\text{H}_2\text{L}^2$ : yield 92%, m.p. 214-216 °C. Anal. Calcd. for  $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_3$ : C: 76.46; H: 4.94; N: 6.86. Found: C: 76.30; H: 4.81; N: 6.94%. Main IR ( $\text{KBr}, \text{cm}^{-1}$ ): 1623 (C=N), 1616 (C=C), 1310 and 1294 (C-O).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , internal

reference TMS):  $\delta$  13.24 (2H, s, O...H...N), 8.65 (2H, s, CH=N), 7.42–7.36 (4H, m, sal-ald), 7.31 (4H, ddd, aminophenyl), 7.09 (4H, ddd, aminophenyl), 7.03 (2H, d, sal-ald), 6.95 (2H, td, sal-ald).

#### 2.4. Electrode Preparation

The general procedure to prepare the PVC membrane was as follow: Different amounts of the ionophore along with appropriate amount of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF) and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 10 h. The tube was then filled with an internal filling solution ( $1.0 \times 10^{-3}$  M  $\text{SmCl}_3$ ). The electrode was finally conditioned for 24 h by soaking in a  $1.0 \times 10^{-3}$  M  $\text{Sm}(\text{NO}_3)_3$  solution [32-34].

#### 2.5. Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements; Ag–AgCl | internal solution,  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>  $\text{SmCl}_3$  | PVC membrane | sample solution | Hg–Hg<sub>2</sub>Cl<sub>2</sub>, KCl (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at  $25.0 \pm 0.1$  °C.

### 3. RESULTS AND DISCUSSION

#### 3.1. Complexation Study

Complexation can actually be defined as a simple interaction between a donor (ligand) and an acceptor (substrate). The characteristics of a ligand and the substrates are important in molecular recognition, because the selective bonding between the ligand and the substrate originates from the information is stored in the ligand and is read out by the substrate. This characteristic information helps define the stability, selectivity, reactivity and transport of the complexes [6,11].

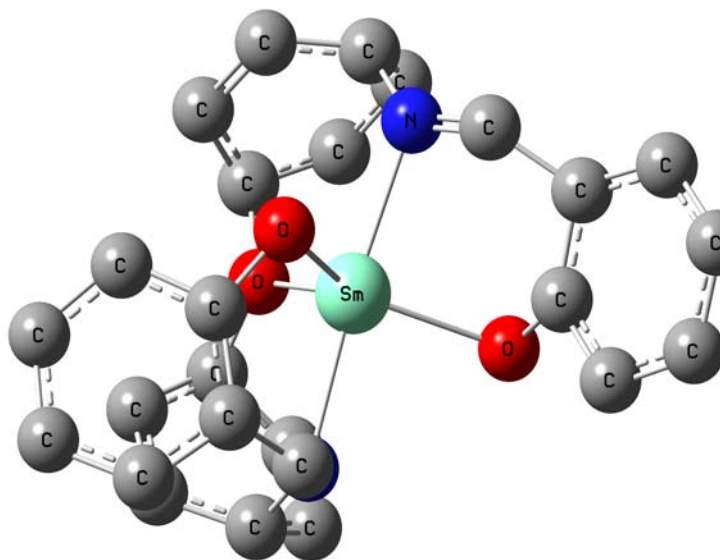
##### 3.1.1. Theoretical Calculations

Many experimental and theoretical investigations have been carried out to understand better the fundamental interaction between metal ions and neutral molecules and their relationship to molecular recognition. Computational models capable of reliably predicting ligand selectivity in a variety of cations have been shown to be valuable tools for the advancement of practical works [35-42]. In order to have a clear picture about the selectivity of the ligand for various metal ions, its binding to some

monovalent, divalent and trivalent ions were investigated by using the Extended Hückel semi-empirical calculations. Because system contains lanthanide atoms, which have not been assigned any basis function in ab-initio calculation, Extended Hückel semi-empirical calculations have been used [43,44]. The influence of the nature, size and charge of metal ions on the complexation reaction with the neutral ligand is explained on the basis of the calculation of gas phase binding energies.

**Table 1.** Interaction energy between metal ions – ligand (APOPIB)

Ion	Interaction Energy (kJ/mol)	Ion	Interaction Energy (kJ/mol)
Sm <sup>3+</sup>	-546.111	Cu <sup>2+</sup>	-79.458
Tm <sup>3+</sup>	-358.065	Co <sup>2+</sup>	-79.672
Gd <sup>3+</sup>	-346.742	Pb <sup>2+</sup>	-74.997
Eu <sup>3+</sup>	-216.232	Zn <sup>2+</sup>	-18.140
La <sup>3+</sup>	-135.658	Ni <sup>2+</sup>	-84.182
Yb <sup>3+</sup>	-133.588	Ag <sup>+</sup>	-4.686
Tb <sup>3+</sup>	-196.073	K <sup>+</sup>	-79.859
Ce <sup>3+</sup>	-123.795	Na <sup>+</sup>	-80.236
Cd <sup>2+</sup>	-5.321	Li <sup>+</sup>	-81.792



**Fig. 2.** Optimal conformation of ligand after complexation with Sm(III)

The binding energy of the uncomplexed ligand and its complexes with metal ions were carried out using Hyper Chem software (Version 6.01). The binding energy ( $\Delta E$ ) was calculated using equation (1):

$$\Delta E = \Delta E_{\text{complex}} - (\Delta E_{\text{ligand}} - \Delta E_{\text{cation}}) \quad (1)$$

Where,  $\Delta E_{\text{complex}}$ ,  $\Delta E_{\text{ligand}}$  and  $\Delta E_{\text{cation}}$  are the total energies of the complex, uncomplexed ligand and metal ion, respectively. Table 1 summarizes the theoretical data relating the stability of the ligand complexes with metal ions.

Based on the above ab-initio calculation results, ionophore could possibly be used as a suitable ionophore in preparation of a samarium ion-selective membrane microelectrode. The optimized structures of ionophore and Sm(III) complexes are shown in Fig. 2.

### 3.1.2. Conductometric study

In ion recognition, the complexation should be examined, because the ligand selectivity towards the metal ions was ambiguous. For this purpose, initially, the APOPIB interaction with numerous metal ions was monitored conductometrically in an acetonitrile solution [45-48].

In all measurements, the cell should be thermostated at the temperature of 25.0 °C, using a Phywe immersion thermostat. In typical experiments, 25 mL of an ion solution ( $1.0 \times 10^{-4} \text{M}$ ) are placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, it should be noted that both the starting solution and the titrant have the same ion concentration. Then, a known amount of an ionophore or a ligand ( $1.0 \times 10^{-2} \text{M}$ ) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition.

The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved.

The 1:1 binding of the cations with the ionophore can be expressed by the following equilibrium:



The corresponding equilibrium constant,  $K_f$ , is given by

$$K_f = \frac{[\text{ML}^{n+}]}{[\text{M}^{n+}][\text{L}]} \times \frac{f_{(\text{ML}^{n+})}}{f_{(\text{M}^{n+})} f_{(\text{L})}} \quad (3)$$

where,  $[\text{ML}^{n+}]$ ,  $[\text{M}^{n+}]$ ,  $[\text{L}]$  and  $f$  represent the equilibrium molar concentration of the complexes, the free cation, the free ionophore and the activity coefficient of the indicated species, respectively. Under the diluted conditions, the activity coefficient of the unchanged ligand  $f_{(\text{L})}$  can be reasonably assumed to be unity [49]. The use of the Debye–Hückel limiting law of the 1:1 electrolytes [50] leads to the conclusion that  $f_{(\text{M}^{n+})} \approx f_{(\text{ML}^{n+})}$ , so the activity coefficient in Eq. (3) is canceled

out. Therefore, the complex formation constant in terms of the molar conductance can be expressed as [51]:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(A_M - A_{obs})}{(A_{obs} - A_{ML})[L]} \quad (4)$$

where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \quad (5)$$

where,  $A_M$  is the molar conductance of the cation before the addition of the ionophore;  $A_{ML}$  is the molar conductance of the complexes,  $A_{obs}$  the molar conductance of the solution during titration,  $C_L$  the analytical concentration of the added ionophore and  $C_M$  the analytical concentration of the cation salt. The complex formation constant,  $K_f$  and the molar conductance of the complex,  $A_{ML}$ , were obtained by computer fitting the Eqs. (4) and (5) to the molar conductance-mole ratio data, using the nonlinear least-squares program KINFIT [52,53].

**Table 2.** Stability constants of the  $M^{n+}$ -APOPIB complexes

Ion	Log $K_f$	Ion	Log $K_f$
Sm <sup>3+</sup>	5.23 ± 0.24	Cu <sup>2+</sup>	2.13 ± 0.32
Tm <sup>3+</sup>	3.24 ± 0.33	Co <sup>2+</sup>	2.24 ± 0.17
Gd <sup>3+</sup>	3.17 ± 0.21	Pb <sup>2+</sup>	<2.0
Eu <sup>3+</sup>	2.31 ± 0.15	Zn <sup>2+</sup>	<2.0
La <sup>3+</sup>	2.43 ± 0.22	Ni <sup>2+</sup>	<2.0
Yb <sup>3+</sup>	2.32 ± 0.11	Ag <sup>+</sup>	<2.0
Tb <sup>3+</sup>	2.45 ± 0.25	K <sup>+</sup>	<2.0
Ce <sup>3+</sup>	2.76 ± 0.25	Li <sup>+</sup>	<2.0
Cd <sup>2+</sup>	<2.0	Na <sup>+</sup>	<2.0

In this experiment, the ligand to cation mole ratio was equal to 1 in all cases. Then, the formation constant values ( $K_f$ ) of the resulting 1:1 complexes were evaluated (Table 2). From Table 2, it was concluded that APOPIB was an appropriate ion carrier for the Sm(III) membrane sensor design.

### 3.2. Membrane composition effect on the potential response of the sensor

Because the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane ingredients, the membrane composition influence on the potential responses of the Sm(III) sensor was inspected [54-60]. In this study, different membrane compositions as shown in Table 3 were tested. As it can be seen, the membrane with the composition of 30% PVC, 5% APOPIB, 3%

NaTPB and 62% NB (no. 6) was the optimum one in the development of this sensor. This membrane composition was selected after many considerations.

**Table 3.** The optimization of the membrane ingredients

Membrane No.	Composition (%)				Slope (mV per decade)
	PVC (%w)	Plasticizer (%w)	ionophore (%w)	Aditive (%w)	
1	30	NB, 64	4	-----	13.2 ± 0.3
2	30	NB, 65	5	-----	17.1 ± 0.4
3	30	NB, 64	6	-----	15.7 ± 0.2
4	30	NB, 62	6	1 (NaTPB)	18.2 ± 0.3
5	30	NB, 62	6	2 (NaTPB)	18.9 ± 0.4
<b>6</b>	<b>30</b>	<b>NB, 62</b>	<b>5</b>	<b>3 (NaTPB)</b>	<b>19.3 ± 0.3</b>
7	30	DBP, 62	5	3 (NaTPB)	17.4 ± 0.2
8	30	BA, 62	5	3 (NaTPB)	18.6 ± 0.5
9	30	NB, 67	0	2 (NaTPB)	3.8 ± 0.3

The high Sm(III) ion extraction into the liquid membrane was a result of the elevated ionophore tendency to form a selective complex with the Sm(III) ions. From Table 3, it was obvious that in the ionophore absence and the existence of other components (no. 9), the response of the recommended electrode was low (slope of  $3.8 \pm 0.3$  mV per decade).

The second factor which helps Sm(III) to extract from an aqueous solution to the membrane as an organic phase is a plasticizer. After the evaluation of three solvent mediators (NB, BA and DBP), it was observed that NB is better plasticizer and membrane with this plasticizer shows better response. Thus, NB was chosen to be employed in the sensor construction, because NB has higher dielectric constant values than other used plasticizer, leading to the better extraction of the high charge density Sm(III).

The presence of lipophilic anions in a cation selective membrane was also considered. Actually, the presence of such anions in a cation selective membrane, which is based on a neutral carrier, decreases the ohmic resistance and improves the response behavior and selectivity. Furthermore, when the extraction capability is poor, it increases the membrane electrode sensitivity [61-65]. Here, a NaTPB addition of 2% as additive led to the slope increase of the potential sensor response from the sub Nernstian value of  $17.1 \pm 0.4$  mV per decade (no. 2) to the Nernstian value of  $19.3 \pm 0.3$  mV per decade (no. 6).

### 3.3. pH effect on the electrode response

In an approach to understanding the impact of pH on the electrode response, the potential was measured at two particular concentrations of Sm(III) solution ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup> and  $1.0 \times 10^{-4}$  mol L<sup>-1</sup>) from the pH value of 2.0 to 12.0 (concentrated NaOH or HCl solutions were employed for the pH



adjustment). In agreement with the resulting data, the potential remained constant despite the pH change in the range of 5.5 to 9.5, indicating the applicability of this electrode in the specific pH range.

On the contrary, relatively fluctuations in the potential vs. pH behavior took place below and above the formerly stated pH limits. The fluctuations above the pH value of 9.5 might be justified by the formation of the soluble and insoluble Sm(III) ion hydroxy complexes in the solution, such as  $\text{Sm}(\text{OH})^{2+}$ ,  $\text{Sm}(\text{OH})_2^+$  and  $\text{Sm}(\text{OH})_3$ . And the fluctuations below the pH value of 5.5 were attributed to the partial protonation of the employed ionophore [66-68].

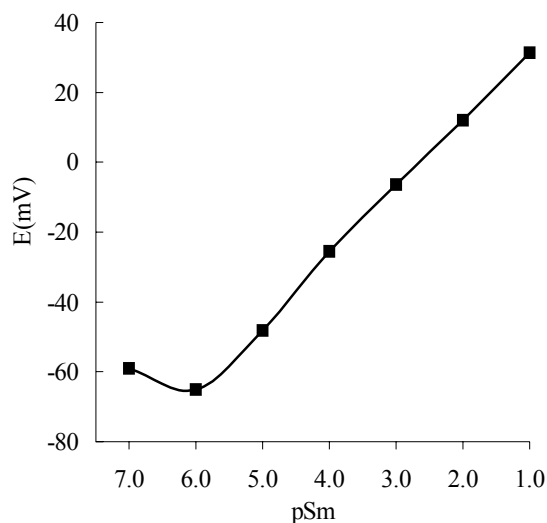
### 3.4. Study of sensor properties

The properties of an ion selective electrode are characterized by parameters like these:

- (1) Measuring range
- (2) Detection limit
- (3) Response time
- (4) Selectivity
- (5) Lifetime
- (6) Accuracy

#### 3.4.1. Measuring range

The measuring range of an ion selective electrode includes the linear part of the calibration graph as shown in Fig. 3. Measurements can be performed in this lower range but it must be noted that more closely spaced calibration points are required for more precise determinations. For many electrodes the measuring range can extend from 1 molar down to  $10^{-6}$  or even  $10^{-7}$  molar concentrations [69,70]. According to another definition, the measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits. The applicable measuring range of the proposed sensor is between  $1 \times 10^{-6}$  and  $1 \times 10^{-1}$  mol L<sup>-1</sup>.



**Fig. 3.** The calibration curve of Sm(III) membrane sensor (membrane no. 6).

### 3.4.2. Detection limit

By extrapolating the linear parts of the ion selective calibration curve, the detection limit of an ion selective electrode can be calculated. In practice, detection limits for the most selective electrodes are in the range of  $10^{-5}$ – $10^{-6}$  mol L<sup>-1</sup>. However, recent studies, have shown that even sub-nM detection limits can be obtained for these devices by different methods such as application of metal buffers to eliminate the contamination of very dilute solutions, using cation-exchange resin in the internal solution of ISEs to keep the primary ion activity at a constant low level, using lipophilic particles such as silica-gel 100 C18-reversed phase into the sensing membrane, using sandwich membranes, and so on [71,72].

In this work the detection limit of the proposed membrane sensor was  $6.1 \times 10^{-7}$  M which was calculated by the extrapolating of the two segment of the calibration curve (Fig. 3).

In comparison with other reported Sm(III) membrane sensors, Table 4 [73-79], the proposed sensor is superior in terms of selectivity coefficients to the previously reported ones.

**Table 4.** Characterization of the proposed Sm(III) membrane sensor and the previous reported ones

Slope (mV per decade)	Linear Range (mol L <sup>-1</sup> )	Detection Limit (mol L <sup>-1</sup> )	Most Important Interfering ions (log K <sub>sel</sub> > -2)	Ref.
19.6	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	$3.1 \times 10^{-6}$	Ce <sup>3+</sup> , La <sup>3+</sup> , Gd <sup>3+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup> , Zn <sup>2+</sup>	73
19.6	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	$8.0 \times 10^{-6}$	Gd <sup>3+</sup>	74
19.8	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$7.0 \times 10^{-7}$	Pb <sup>2+</sup> , Ce <sup>3+</sup>	75
19.3	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	$8.0 \times 10^{-6}$	Pb <sup>2+</sup>	76
19.3	$10^{-6}$ - $10^{-1}$	$5.5 \times 10^{-7}$	Yb <sup>3+</sup> , Ag <sup>+</sup>	77
19.3	$10^{-6}$ - $10^{-1}$	$6.1 \times 10^{-7}$	Gd <sup>3+</sup>	78
40 (Super Nernstian)	$10^{-5}$ - $10^{-1}$	$1.0 \times 10^{-5}$	Pr <sup>3+</sup> , Ca <sup>2+</sup>	79
19.3	$10^{-6}$ - $10^{-1}$	$6.1 \times 10^{-7}$	-	This work

### 3.4.3. Response time

The response time of an electrode, is evaluated by measuring the average time required to achieve a potential within  $\pm 0.1$  mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions, like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before performing the experiment measurement, any previous usages or preconditioning of the electrode, and the testing temperature, are effective on the experimental response time of a sensor [81-84].

In this work, less than 10s response time was obtained for the proposed electrode when contacting different Sm(III) solutions from  $1.0 \times 10^{-3}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup>, and about 15 s in low concentration solutions which is due to the effect of analyte concentration on the response time of ion selective electrode.

### 3.4.4. Selectivity

Selectivity, which describes an ion selective electrodes specificity toward the target ion in the presence of interfering ions, is the most important characteristics of these devices. The potentiometric selectivity coefficients of the Sm(III) sensor were evaluated by the matched potential method (MPM) and separated solution method (SSM) [85]. According to the Bakker et al. recommendation [40], the selectivity coefficient also was evaluated by modified separated solution method (MSSM). To eliminate the bias which is caused by ion leaching from the membrane, the membrane that had not been contacted with primary ion was used [86-88].

The resulting values of the selectivity coefficients are given in Table 5. As can be seen from Table 5, for the all mono and bivalent metal ions and trivalent lanthanide ions tested, the selectivity coefficients are about  $10^{-3}$ , which seems to indicate negligible interferences in the performance of the electrode assembly. As it can be seen from the results of three used method, there is a difference among the selectivity coefficient calculated by MPM or SSM with MSSM. The MSSM provide unbiased selectivity coefficients allow accurate predictions of the electrode response to real samples [87].

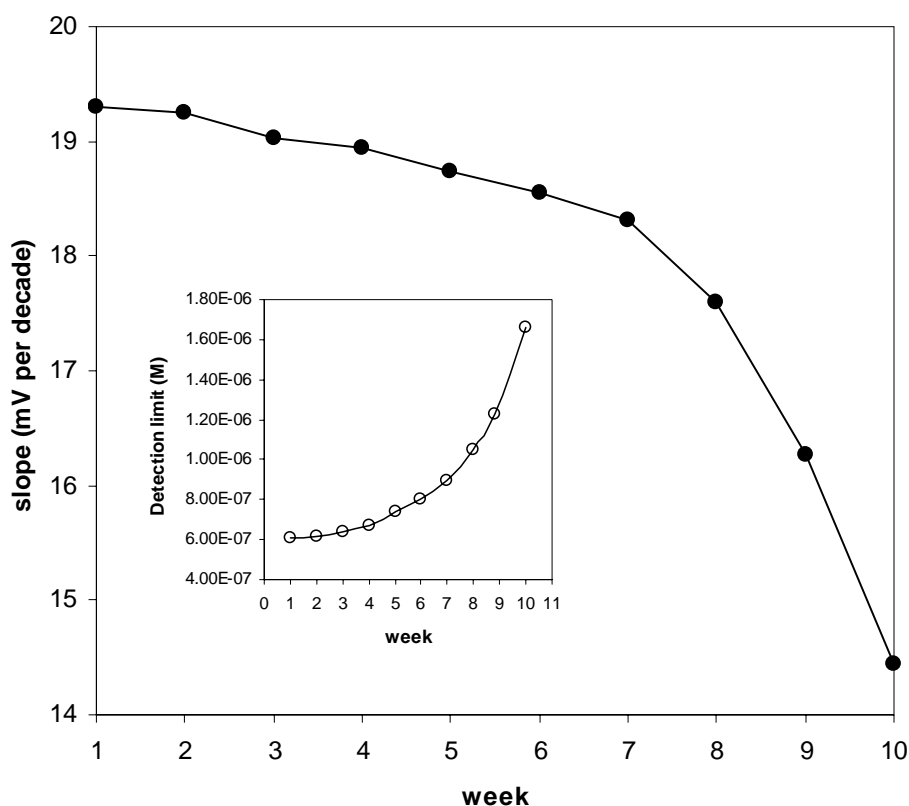
**Table 5.** The selectivity coefficients of various interfering cations for the membrane no. 6

Ion	Log $K_{MPM}$	Log $K_{SSM}$	Log $K_{MSSM}$
Li <sup>+</sup>	-3.3	-3.2	-4.1
Na <sup>+</sup>	-3.4	-3.5	-4.3
K <sup>+</sup>	-3.2	-3.4	-4.2
Ag <sup>+</sup>	-4.1	-4.2	-4.9
Mg <sup>2+</sup>	-3.1	-3.0	-4.3
Ca <sup>2+</sup>	-2.9	-3.2	-3.9
Cd <sup>2+</sup>	-4.1	-4.2	-5.0
Pb <sup>2+</sup>	-3.3	-3.3	-4.3
Ni <sup>2+</sup>	-3.2	-3.0	-4.3
Zn <sup>2+</sup>	-3.2	-3.3	-4.0
Cu <sup>2+</sup>	-4.1	-3.9	-4.8
La <sup>3+</sup>	-3.1	-3.1	-4.1
Ce <sup>3+</sup>	-3.2	-3.2	-5.0
Pr <sup>3+</sup>	-3.2	-3.3	-4.8
Nd <sup>3+</sup>	-3.0	-3.1	-4.0
Sm <sup>3+</sup>	-3.4	-3.6	-4.3
Eu <sup>3+</sup>	-3.1	-3.1	-4.5
Gd <sup>3+</sup>	-2.3	-2.5	-3.7
Tb <sup>3+</sup>	-3.3	-3.2	-4.2
Dy <sup>3+</sup>	-3.9	-3.7	-5.2
Er <sup>3+</sup>	-3.2	-3.4	-4.8
Tm <sup>3+</sup>	-1.8	-2.1	-3.2
Yb <sup>3+</sup>	-3.1	-3.1	-4.2
Lu <sup>3+</sup>	-3.3	-3.0	-4.1

Also, there is a good correspondence between the formation constants and the selectivity coefficients orders, because the selectivity of an ion selective sensor is mainly related to the stability of the complex between ion and ionophore.

### 3.4.5. Lifetime

The average lifetime for most of the reported ion selective sensors is in the range of 4–10 weeks. After this time the slope of the sensor will decrease, and the detection limit will increase. They were tested for a period of 10 weeks, during which the electrodes were used extensively (one hour per day). Fig. 4 shows the changes in the slope and detection limits of a sensor with time. The proposed sensors can be used for 7 weeks. Firstly, a slight gradual decrease in the slopes (from 19.3 to 18.3 mV per decade) and, secondly, an increase in the detection limit (from  $6.1 \times 10^{-7}$  mol L<sup>-1</sup> to  $7.0 \times 10^{-6}$  mol L<sup>-1</sup>). It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for limited lifetimes of the sensors.



**Fig. 4.** The lifetime of the Sm(III) membrane sensor (membrane no. 6)

### 3.4.6. Accuracy

To evaluate the accuracy of the proposed sensor, the sensor was successfully applied to direct monitoring of 10 g/L of Sm(III) in certified reference material, samarium ICP/DCP standard solution

in 10% HNO<sub>3</sub> and the results showed that recovery of Sm(III) ions is very good (100.2%-102.3%). These experimental data revealed that the proposed electrode performed a trustworthy detection of the Sm(III) ions.

#### 4. CONCLUSIONS

The special radius range of the lanthanide ions defines particular properties for these elements (charge densities, size, and hydration energy). As a consequence, the design of a new highly selective lanthanide ion sensor was based on the selection of a suitable plasticizer as well as a suitable ionophore, with a semi-cavity and a relatively high flexibility.

Complexation of a new bis-bidentate schiff's base, 2-[[4-[[3-[[z)-1-(2-hydroxy phenyl) methylidene] amino]phenyl]oxy]phenyl]imino) methyl]-1-benzenol (APOPIB) with some mono, di and trivalent metal ions was investigated by the theoretical calculations and conductance studies. Since APOPIB was able to form a selective complex with Sm(III) ion ( $K_f=5.23 \pm 0.24$ ), it was applied as a sensing material in a poly vinyl chloride (PVC) membrane sensor for determination of Sm(III) ions.

The proposed sensor exhibited a fast response time, a lower detection limit of  $6.1 \times 10^{-7}$  M and pH independent potential responses across the range of 5.5–9.5. Its selectivity towards the samarium ions was not influenced by the presence of the common alkali, alkaline earth, transition and heavy metal ions, since their interference was low. For the assessment of the electrode performance, a Certified Reference Material (CRM) was used.

#### ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the Research Council of University of Tehran for the financial support of these investigations.

#### References

1. S. P. Fricker, *Chem. Soc. Rev.*, 35 (2006) 524.
2. A. Mazzucotelli, F. Depaz, E. Magi, B. Frache, *Anal. Sci.*, 8 (1992) 189.
3. S. Larach, R. E. Shrader, R. A. Kauffunger, *Anal. Chim. Acta*, 51 (1970) 409.
4. R. Q. Aucélio, C. L. V. Johnson, B. W. Smith, J. D. Winefordner, *Anal. Chim. Acta*, 411 (2000) 57.
5. F. Faridbod, M. R. Ganjali, R. Dinarvand, P. Norouzi, *Combinatorial Chemistry & High Throughput Screening*, 10 (2007) 527.
6. F. Faridbod, M. R. Ganjali, P. Norouzi, *Sensors*, 8 (2008) 1645.
7. M. R. Ganjali, P. Norouzi, F. Faridbod, M. Rezapour, M. R. Pourjavid, *J. Iran. Chem. Soc.*, 4 (2007) 1.
8. F. Faridbod, M. R. Ganjali, R. Dinarvand, P. Norouzi, *African J. Biotechnol.* 6 (2007) 2960.
9. M. Javanbakht, M. R. Ganjali, P. Norouzi, M. Abdouss, S. Riahi, *Anal. Lett.* 41 (2008) 619.
10. N. N. Greenwood, A. Earnshaw, *Chemistry of the elements*, Pergamon, 1984.
11. M. R. Ganjali, F. Faridbod, P. Norouzi, M. Adib, *Sens. Actuators B*, 120 (2006) 119.
12. M. R. Ganjali, P. Norouzi, M. Rezapour, F. Faridbod, M. R. Pourjavid, *Sensors*, 6 (2006) 1018.

13. M. R. Abedi, H. A. Zamani, M. R. Ganjali, P. Norouzi, *Intern. J. Environ. Anal. Chem.* 88 (2008) 353.
14. M. R. Ganjali, P. Norouzi, F. S. Mirnaghi, S. Riahi, F. Faridbod, *IEEE Sens. J.* 7 (2007)1138.
15. M. R. Ganjali, R. Kiani-Anbouhi, M. Shamsipur, T. Poursaberi, M. Salavati-Niasari, Z. Talebpour, M. Emami, *Electroanalysis*, 16 (2004)1002.
16. V. K. Gupta, A. K. Singh, B. Gupta, *Anal. Bioanal. Chem.*, 390 (2008) 2171.
17. T. Ito, C. J. Coto, *Trace. Microprobe Tech.* 19 (2001) 601.
18. M. Shamsipur, S. Ershad, N. Samadi, A. R. Esmaeilbeig, R. Kia, A. Abdolmaleki, *Electroanalysis*, 17 (2005) 1828.
19. M. R. Ganjali, P. Norouzi, T. Alizadeh, A. Tadjarodi, Y. Hanifehpour, M. Adib, *Electroanalysis*, 18 (2006) 1091.
20. S. Khalil, *Anal. Lett.*, 36 (2003) 1335.
21. V. K. Gupta, A. K. Singh, B. Gupta, *Anal. Chim. Acta*, 575 (2006) 198.
22. H. A. Zamani, M. R. Ganjali, P. Norouzi, S. Meghdadi, *J. Appl. Electrochem.*, 37 (2007) 853.
23. S. K. Mittal, S. K. A. Kumar, H. K. Sharma, *Talanta*, 62 (2004) 801.
24. M. Akhond, B. Najafi, J. Tashkhourian, *Anal. Chim. Acta*, 531(2005) 179.
25. M. R. Ganjali, P. Norouzi, N. Yousefian, F. Faridbod, M. Adib, *Bull. Korean Chem. Soc.*, 27 (2006) 1581.
26. H. A. Zamani, M. R. Ganjali, P. Norouzi, M. Adib, M. Aceedy, *Anal. Sci.*, 22 (2006) 943.
27. T. Ito, C. Goto, K. Noguchi, *Anal. Chim. Acta*, 443 (2001) 41.
28. H. Karami, M. F. Mousavi, M. Shamsipur, I. Yavari, A. A. Alizadeh, *Anal. Lett.*, 36 (2003) 1065.
29. M. Akhond, M. B. Najafi, J. Tashkhourian, *Sens. Actuators B*, 99 (2004) 410.
30. H. A. Zamani, M. R. Ganjali, M. Adib, *Sens. Actuators B*, 120 (2007) 545.
31. A. A. A. Gaber, *Anal. Lett.*, 36 (2003) 2585.
32. M. R. Ganjali, F. Mirnaghi, P. Norouzi, M. Adib, *Sens. Actuators B*, 115 (2006) 374.
33. P. Norouzi, M. R. Ganjali, A. Ahmadalinezhad, M. Adib, *J. Brazil. Chem. Soc.*, 17 (2006)1309.
34. H. A. Zamani, G. Rajabzadeh, M. R. Ganjali, P. Norouzi, *Anal. Chim. Acta*, 598 (2007) 51.
35. M. A. Thompson, E. D. Glendening, D. Feller, *J. Phys. Chem.*, 98 (1994) 10465.
36. E. D. Glendening, D. Feller, M. A. Thompson, *J. Am. Chem. Soc.*, 116 (1994) 10657.
37. L. X. Dang, P. A. Kollman, *J. Am. Chem. Soc.*, 112 (1990) 5716.
38. M. R. Ganjali, P. Norouzi, F. Faridbod, S. Riahi, J. Ravanshad, J. Tashkhourian, M. Salavati-Niasari, M. Javaheri, *IEEE Sensor J.*, 7 (2007) 544.
39. M. S. Islam, R. A. Pethrick, D. Pugh, M. J. Wilson, *J. Chem. Soc. Faraday Trans.*, 93 (1997)387.
40. F. Faridbod, M. R. Ganjali, B. Larijani, P. Norouzi, S. Riahi, F. S. Mirnaghi, *Sensors*, 7 (2007) 3119.
41. M. R. Ganjali, P. Norouzi, F. Faridbod, S. Riahi, M. R. Yaftian, A. Zamani, D. Matt, *J. Appl. Electrochem.*, 37 (2007) 827.
42. M. R. Ganjali, P. Norouzi, B. Akabri-Adergani, S. Riahi, B. Larijani, *Anal. Lett.*, 40 (2007) 1923.
43. R. J. Hoffmann, *Chem. Phys.*, 39 (1963) 1397.
44. R. Hoffmann, W. N. Lipscomb, *J. Chem. Phys.*, 38 (1962) 2179.
45. M. R. Abedi, H. A. Zamani, M. R. Ganjali, P. Norouzi, *Sensor Lett.*, 5 (2007) 516.
46. M. J. Pooyamanesh, H. A. Zamani, G. Rajabzadeh, M. R. Ganjali, P. Norouzi, *Anal. Lett.*, 40 (2007) 1596.
47. H. A. Zamani, G. Rajabzadeh, M. R. Ganjali, *Sens. Actuators B* 119 (2006) 41.
48. Y. Takeda, *Bull. Chem. Soc. Japan*, 56 (1983) 3600.
49. M. R. Ganjali, N. Khoshdan, O. R. Hashemi, S. A. S. Sajjadi, *Pol. J. Chem.*, 74 (2000)1389-1398.
50. Z. Pourghobadi, F. Seyyed-Majidi, M. Daghighi-Asli, F. Parsa, A. Moghimi, M. R. Ganjali, H. Aghabozorg, M. Shamsipur, *Pol. J. Chem.*, 74 (2000) 837.
51. M. R. Ganjali, A. Rouhollahi, A. R. Mardan, M. Shamsipur, *J. Chem. Soc-Faraday Trans.*, 94 (1998) 1959.

52. V. A. Nicely, J. L. Dye, *J. Chem. Educ.*, 48 (1971) 443.
53. D. P. Zollinger, E. Bulten, A. Christenhusz, M. Bos, W. E. VanderLinden, *Anal. Chim. Acta*, 198 (1987) 207.
54. M. R. Ganjali, J. Ravanshad, M. Hosseini, M. Salavati-niasari, M. R. Pourjavid, M. R. Baezzat, *Electroanalysis*, 16 (2004)1771.
55. V. K Gupta, S. Jain, S. Chandra, *Anal. Chim. Acta*, 486 (2003) 199.
56. M. R. Ganjali, A. Ghesmi, M. Hosseini, M. R. Pourjavid, M. R. Rezapour, M. Shamsipur, M. Salavati-Niasari, *Sens. Actuators B*, 105 (2005) 334.
57. P. Buhlmann, E. Pretsch, E. Bakker, *Chem. Rev.*, 98 (1998) 1593.
58. V. K.Gupta, S. Chandra, R. Mangla, *Sens. Actuators B*, 86 (2002) 235.
59. M. R. Ganjali, S. Rasoolipour, M. Rezapour, P. Norouzi, M. Adib, *Electrochem. Commun.*, 7 (2005) 989.
60. V. K. Gupta, R. Prasad, A. Kumar, *Talanta*, 63 (2004) 1027.
61. W. Szczepaniak, M. Ren, *Talanta*, 41 (1994) 1393.
62. M. R. Ganjali, S. Rasoolipour, M. Rezapour, P. Norouzi, A. Tajarodi, Y. Hanifehpour, *Electroanalysis*, 17 (2005) 1534.
63. M. R. Ganjali, M. Rahimi, B. Maddah, A. Moghimi, S. Borhany, *Anal. Sci.*, 20 (2004) 1427.
64. M. Shamsipur, M. Yousefi, M. Hosseini, M. R. Ganjali, *Anal. Chem.*, 74 (2002) 5538.
65. M. R. Ganjali, M. Tahami, M. Shamsipur, T. Poursaberi, S. Haghgoo, M. Hosseini, *Electroanalysis*, 15 (2003) 1038.
66. M. F. S. Teixeira, O. Fatibello-Filho, L. A. Ramos, *Quim. Nova*, 28 (2005) 817.
67. R. K. Mahajan, I. Kaur, V. Sharma, M. Kumar, *Sensors*, 2 (2002) 417.
68. M. R. Ganjali, A. Daftari, F. Faridbod, P. Norouzi, M. Salavati-Niasari, *Sens. Actuators B*, 120 (2007) 673.
69. V. K. Gupta, S. Chandra, S. Agarwal and H. Lang, *Sens. Actuators B*, 107 (2005) 762.
70. A.K. Jain, V.K. Gupta, S. Radi, L.P. Singh and J.R. Raison, *Electrochimica Acta*, 51(12), 2547-2553(2006).
71. A. C. Ion, E. Bakker, E. Pretsch, *Anal. Chim. Acta*, 440 (2001) 71.
72. S. Peper, A. Ceresa, E. Bakker, *Anal. Chem.*, 73 (2001) 3768.
73. M. Shamsipur, M. Hosseini, K. Alizadeh, M. M. Eskandari, H. Sharghi, M. F. Mousavi, M. R. Ganjali, *Anal. Chim. Acta*, 486 (2003) 93.
74. M. Shamsipur, M. Hosseini, K. Alizadeh, Z. Talebpour, M. F. Mousavi, M. R. Ganjali, M. Arca, V. Lippolis, *Anal. Chem.*, 75 (2003) 5680.
75. M. R. Ganjali, M. R. Pourjavid, M. Rezapour, S. Haghgoo, *Sens. Actuators B*, 89 (2003) 21.
76. M. R. Ganjali, M. Rezapour, M. R. Pourjavid, S. Haghgoo, *Anal. Sci.*, 20 (2004) 1007.
77. Zamani, H. A.; Ganjali, M. R.; M. Adib, *J. Braz. Chem. Soc.*, 18 (2007) 215.
78. M. B. Saleh, A. A. A. Gaber, M. M. R. Khalaf, A. M. Tawfeek, *Anal. Lett.*, 39 (2006) 17.
79. S. K. Mittal, H. K. Sharma, A. S. K. Kumar, *Sensors*, 4 (2004) 125.
80. H. A. Zamani, J. Abedini-Torghabeh, M. R. Ganjali, *Electroanalysis*, 18 (2006) 888.
81. A. K. Singh, V. K. Gupta, B. Gupta, *Anal. Chim. Acta*, 585 (2007) 171.
82. S. Riahi, M. F. Mousavi, S. Z. Bathaie, M. Shamsipur, *Anal. Chim. Acta*, 548 (2005) 192.
83. V. K. Gupta, A. K. Singh, M. Al Khayat, B. Gupta, *Anal. Chim. Acta*, 590 (2007) 81.
84. V. K. Gupta, A. K. Jain and G. Maheshwari, *Int. J. Electrochem. Sci.*, 2 (2007) 102.
85. P. R. Buck, E. Lindner, *Pure & Appl. Chem.* 66 (1994) 2527.
86. E. Bakker, E. Pretsch, P. Bulhmann, *Anal. Chem.*, 72 (2000) 1127.
87. E. Bakker, *Anal. Chem.*, 69 (1997)1061.
88. Y. Umezawa, K. Umezawa, H. Sato, *Pure & Appl. Chem.*, 67 (1995) 507.